INCORPORATING CERAMIC MANUFACTURING WASTE AND RECYCLED GLASS INTO THE INTEGRAL CERAMIC PROCESS

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ABSTRACT

The following research paper explains the results obtained when waste generated by the ceramic sector, such as chamotte from fired porcelain tile scrap and unfired scrap, sludge and water from the washing stage, together with waste from other sectors such as recycled glass, is used to design an engobe and glaze to produce an integral ecological tile.

1. INTRODUCTION

Nowadays, recycling the products we consume has become an inevitable requirement in order to optimise consumption of natural resources while simultaneously preventing pollution from the disposal of such waste.

Recycled glass can come from several sources, such as flat glass, glass bottles, light-bulbs, television screens, etc. Before it can be used in ceramic tile manufacturing, it has to provide certain characteristics: supply needs to be plentiful and its composition must be both homogenous and constant.

Most types of glass are made up of network-forming oxides and network-modifying oxides, the bases of which are principally either silicon oxide, calcium oxide or sodium oxide. In its glassy state, the structure is seen to be disordered, where the positions of the atoms are not correlated and with a chaotic behaviour similar to a liquid, so that it displays an amorphous structure. The amorphous nature of glass and also its composition (rich in alkalis) give it a fluxing character. Because of these properties, recycled glass can be used both in ceramic body compositions (where it acts as a flux in a similar way as feldspars do) and in ceramic engobe and glaze compositions as a substitute for frits.

In recent years, the Spanish ceramic industry has undergone a period of crisis and uncertainty, with production levels dropping to 50% in less than three years. But this crisis may also herald new opportunities for the sector by encouraging the development and manufacture of more environmentally friendly, ecological tiles.

The overall objective of this research was to obtain an integral ecological ceramic tile with a high content of recyclable raw materials, which at the same time are by-products of various types of waste from other sectors, such as recycled waste glass, chamotte from fired and unfired ground porcelain tile scrap, sludge generated by the tile making sector itself and water from the washing section.

2. EXPERIMENTAL METHOD EMPLOYED

2.1. Organisation chart of participating companies and institutions

In order to carry out the proposed project, the assistance of the following companies was necessary:

PLAZA CERÁMICAS, a ceramics company located in Alcora (Castellon, Spain), which manufactures the ecological porcelain tiles called EKOLOGIC. This company formulated the compositions and implemented the entire decorating process to successfully produce the end product.

TIERRA ATOMIZADA, a company located in Alcora (Castellon, Spain) which is dedicated to manufacturing ceramic bodies using a spray-drying process for both red and white bodies. This company was where the research into ecological porcelain tile composition formulations was carried out, including testing of the various formulations in their pilot plant, and where the compositions were characterised in their quality control laboratories.

COLORES CERÁMICOS, a company located in Onda (Castellon, Spain) which manufactures ceramic glazes and pigments. Through its subsidiary, MICROCOLORS, it also owns a digital decorating and water-based colour development system. The company participated in producing ecological engobes and glazes in its pilot plant. It also carried out the ecological tile decorating process using a water-based pigment ink-jet system.

CAMACHO RECYCLING: this business group is located in Caudete (Albacete, Spain) where it specialises in the selective collection of used glass and its subsequent treatment for recycling in different production systems. The firm was responsible for preparing the recycled glass waste to be used in different ceramic tile components (body, engobes and glaze). It was also in charge of formulating the various ecological engobes and glazes.

UNIVERSITAT JAUME I: the University's Inorganic and Organic Chemistry department carried out the scientific coordination of the project and also the characterisation of the newly-prepared materials with the assistance and support of the Central Scientific Instrumentation Service. At the same time, the *Instituto de Tecnología Cerámica* (ITC) carried out environmental studies on the formulated bodies and characterisation of the finished tiles according to relevant quality control parameters.

2.2. Physical, chemical and structural characterisation of the materials used

2.2.1. Glass characterisation

First of all, the recycled waste glass was analysed for homogeneity. The entire project was carried out using recycled sodium–calcium glass, the vast majority of which came from recycled flat glass and was therefore most widely available and could offer the ceramics sector a guaranteed supply. Furthermore, to formulate the glazes, waste borosilicate glass, although less widely available, was used. Table 1 shows the detailed chemical analysis of the recycled sodium–calcium oxide flat glass waste.

Component	Concentration (% by weight)
SiO_2	73.2
Al_2O_3	0.85
Na_2O	12.0
MgO	3.75
P_2O_5	0.013
SO_3	0.20
K_2O	0.30
CaO	8.87
TiO_2	0.05
Fe_2O_3	0.099

Table 1. Chemical analysis of a flat glass waste

Figure 1 shows how the sodium–calcium waste glass behaved under heat treatment when analysed through hot stage microscopy.

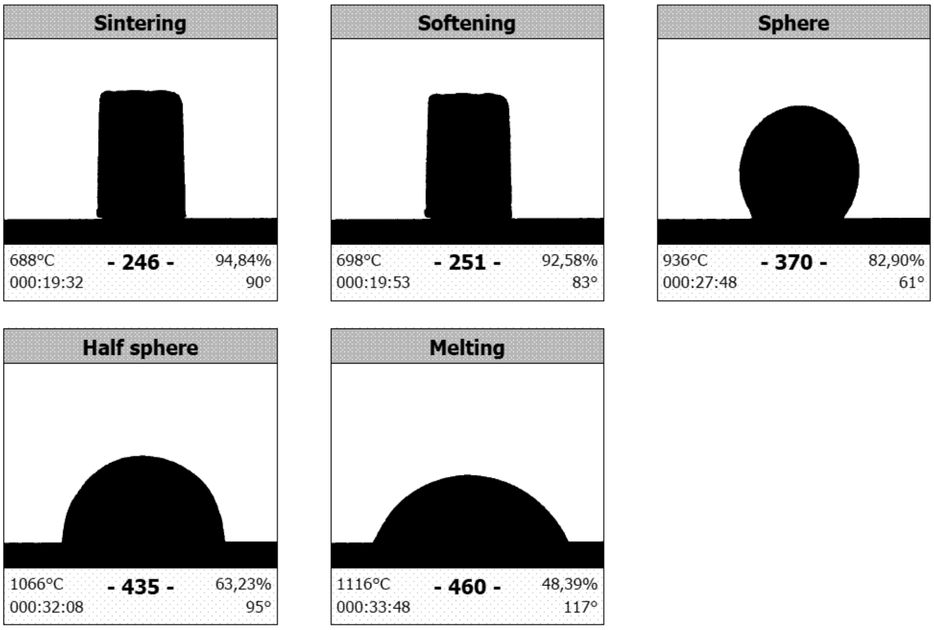

Figure 1 Flat glass waste behaviour under heat treatment when analysed with hot-stage microscopy.

Morphological and micro-analytical characterisation of the recycled flat glass waste was carried out using scanning electron microscopy and X-ray microanalysis (SEM/EDX).

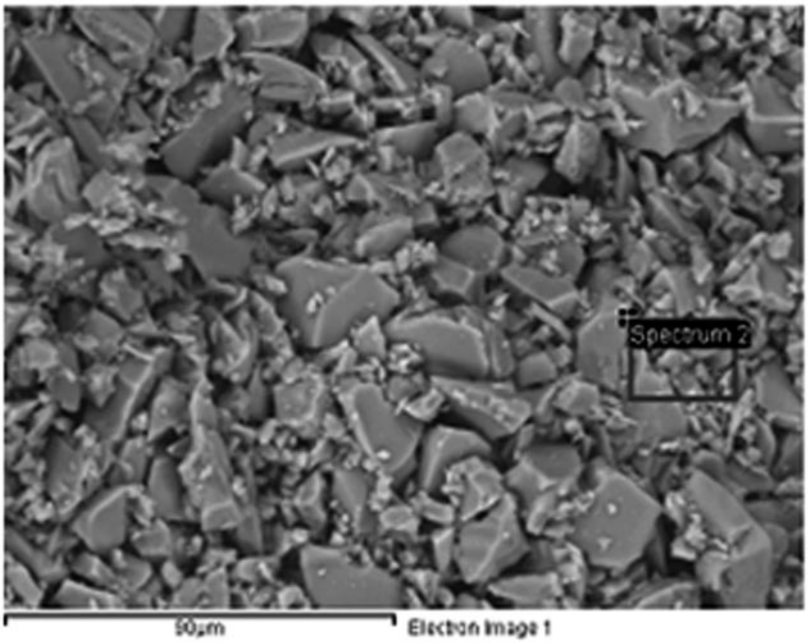

Figure 2. SEM micrograph of a sample of sodium–calcium glass waste.

Special mention should be made of the fact that the analysis was carried out on several observation fields and both the individual and average results demonstrated consistency in the sample composition.

Element	Weight %	Atomic%	Compd %	Formula
Na K	11.51	10.32	15.52	Na_2O
Mg K	2.52	2.14	4.18	MgO
Al K	0.55	0.42	1.04	Al_2O_3
Si K	33.29	24.43	71.22	SiO_2
Ca K	5.75	2.95	8.04	CaO
O	46.38	59.74		

Table 2. Results of the microanalysis performed on the sample of sodium–calcium glass waste.

2.3. Ecological ceramic body formulation

The method employed was to formulate porcelain tile body compositions from mixes of kaolinitic clays (40–45% by weight) feldspar (30–35% by weight) and feldspathic sand (5–10%), together with the recycled material (15–20%). This recycled material contained sodium–calcium glass, chamotte from fired porcelain tile scrap and unfired scrap.

2.4. Ceramic body characterisation

2.4.1. Chemical analysis

Table 3 shows the chemical analysis of the body composition formulated with the reused waste materials.

DATE	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2	MnO	Fe_2O_3	L.O.I.	SUM
12/01/2011	4,77	0,50	19,00	68,45	0,09	1,33	0,88	0,68	0,00	0,69	3,45	99,84

Table 3. XRF chemical analysis of body composition formulated with the waste materials.

2.4.2. Dilatometric analysis

Figure 3 shows the dilatometric curve obtained on a sample of the composition indicated in Table 3.

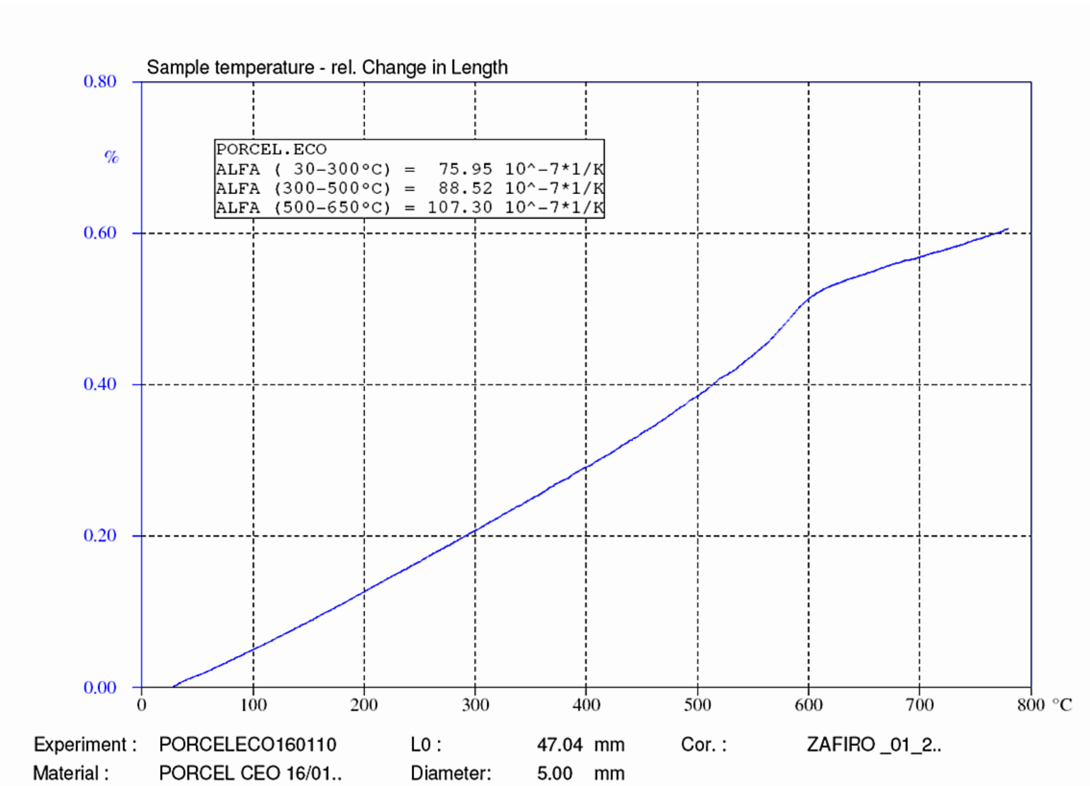

Figure 3. Dilatometric curve corresponding to the ecological body formulated with the materials shown in Table 3.

2.4.3. Vitrification diagram

Figure 4 shows the vitrification diagrams for each body. It also shows how the body behaves under a press pressure of 360 kg/cm², where it gives a bulk density reading of 2.056 g/cm^3 after firing, and 7.56% linear shrinkage and 0.28% water absorption at temperatures of over 1165°C. These values remain practically stable as far as linear shrinkage is concerned up to 1190°C, whereas water absorption decreases to a value of 0.06%.

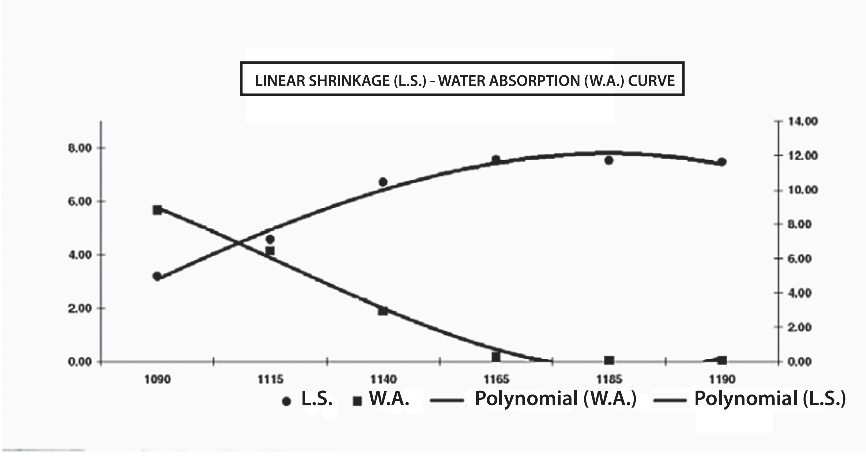

Figure 4. Vitrification diagram and technological variables for the ecological body formulated according to the composition detailed in Table 3.

2.4.4. Particle size analysis

Figure 5 shows the particle size readings obtained for the ceramic processing of the ecological body. The particle size distribution graph shows that 30.99% of the particles are 400 microns in size, 27.94% have a size of 300 microns, 16.38% a size of 500 microns, and 12.46% a size of 200 microns. Then the smallest groups show 5.59% of particles sized 630 microns, 5.21% with a size of 100 microns and finally a small number of particles with a size of 75 microns (0.96%) or less than 75 microns (0.48%).

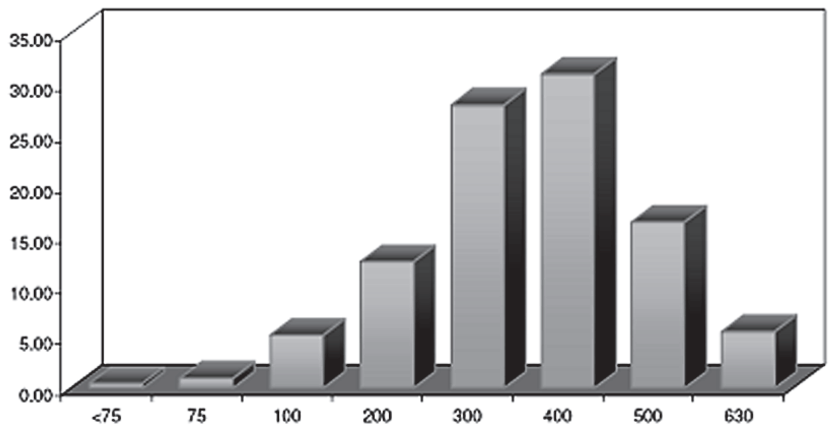

Figure 5. Particle size distribution in the formulated ecological body after the spray-drying stage

2.4.5. Mechanical strength analysis

Mechanical strength was also measured on both fired and unfired pressed compacts of the composition. Thus, for the unfired, dry compacts, bending tensile strength was 3.62 N/mm^2, i.e. at the top end of the range.

2.5. Formulation of a engobe–glaze and satin glaze composition for the experimental porcelain tile body

A type of engobe–glaze, as well as a 'satin' glaze composition, was formulated using the recycled glass waste and chamotte, together with other components, as shown in Table 4. The table shows that in the case of the engobe–glaze, the glass waste used comes from recycled flat glass (sodium–calcium glass), whereas to formulate the glaze composition, two types of recycled glass were used: glass waste designated Reference 1, which was sodium–calcium-based flat glass, and Reference 2, which was borosilicate glass.

Engobe–glaze (GCE-001-10-30)	
Recycled glass waste	10%
Chamotte	11%
Hyplast-67 clay	25%
Kaolin	13%
Zircosil five	7%
Quartz	10%
Calcium carbonate	10%
Sodium feldspar	14%
Cmc	0.1%
KD-8040 (zschimmer)	0.3%

Satin glaze (GCE-001-10-67)	
Recycled glass waste -1	10%
Recycled glass waste -2	5%
Hyplast-67 clay	15%
Kaolin	10%
Zircosil five	8%
Quartz	16%
Calcium carbonate	21%
Sodium feldspar	13%
Zinc oxide	2%
Cmc	0.2%

Table 4. Engobe–glaze and satin glaze formulation

2.5.1. Chemical analysis of the engobe–glaze

A theoretical study of the contents of the materials that constitute the engobe–glaze and the satin glaze indicated in Table 5 was carried out.

ENGOBE–GLAZE CGE-001-10-30	
Na_2O	2.48
K_2O	1.31
CaO	6.97
MgO	0.58
ZnO	-
BaO	-
Al_2O_3	16.13
SiO_2	62.19
B_2O_3	-
ZrO_2	4.52
TiO_2	0.68
Fe_2O_3	0.59
L.O.I.	4.55

SATIN GLAZE CGE-001-10-67	
Na_2O	2.62
K_2O	0.77
CaO	13.22
MgO	0.48
ZnO	1.99
BaO	-
Al_2O_3	9.89
SiO_2	55.27
B_2O_3	0.53
ZrO_2	5.09
TiO_2	0.30
Fe_2O_3	0.29
L.O.I.	9.55

Table 5. Chemical analysis of the engobe–glaze and satin glaze

3. ASSESSMENT OF THE DEGREE OF WASTE REUSE IN THE ECO-LOGIK TILE

The degree to which waste materials were reused to manufacture ECO-LOGIK tiles was analysed with the following results:

For the ceramic body, usage of natural resource-based raw materials (mine extracted) was successfully reduced by 16%. Likewise, reductions of 50% in clean water and 20% in energy consumption were also achieved to make a total aggregate reduction in natural resources and energy of 86%. Figure 6 is a pie chart of the cost savings in natural resources and energy using the process described here.

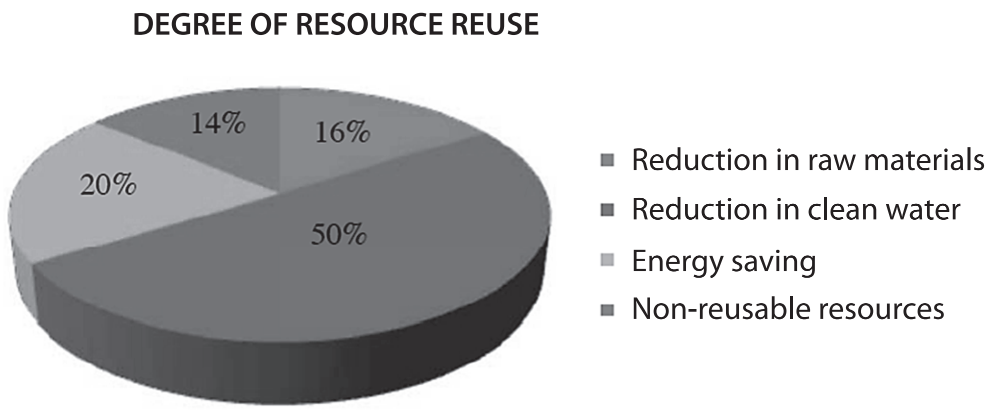

Figure 6. *Distribution of natural resources and energy savings in the development of the ceramic body*

Natural resources saving analysis of the engobe–glaze and satin glaze formulations:

Engobe–glaze. The engobe–glaze was formulated with 11% ground chamotte from the porcelain tile manufacturing process and 10% recycled glass waste. Thus, a total of 21% of the composition comprised waste materials, see Figure 7.

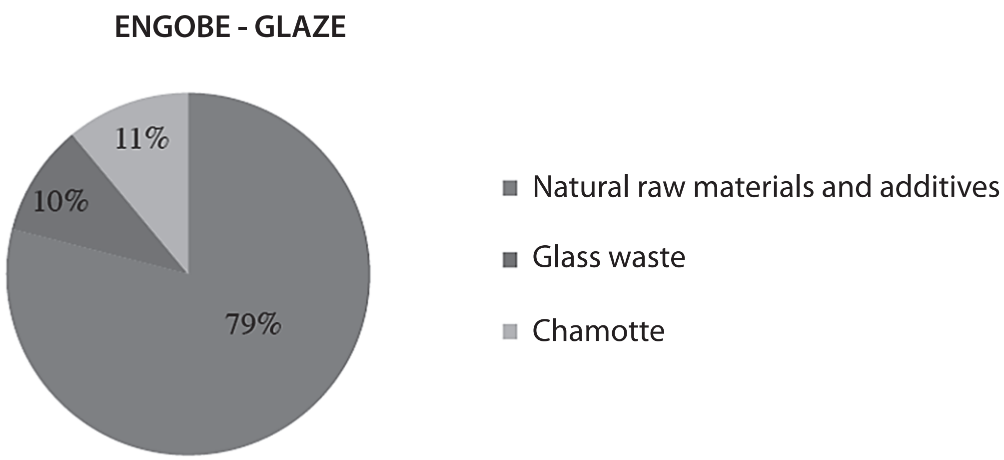

Figure 7. *Distribution of waste materials used to develop an engobe–glaze.*

In formulating the satin glaze, 10% (by weight) of the formula was recycled sodium–calcium glass waste (Glass 1 in Table 4) and 5% was the borosilicate glass (Glass 2 in Table 4), thereby making a total fraction of 15% recycled glass waste, see Figure 8.

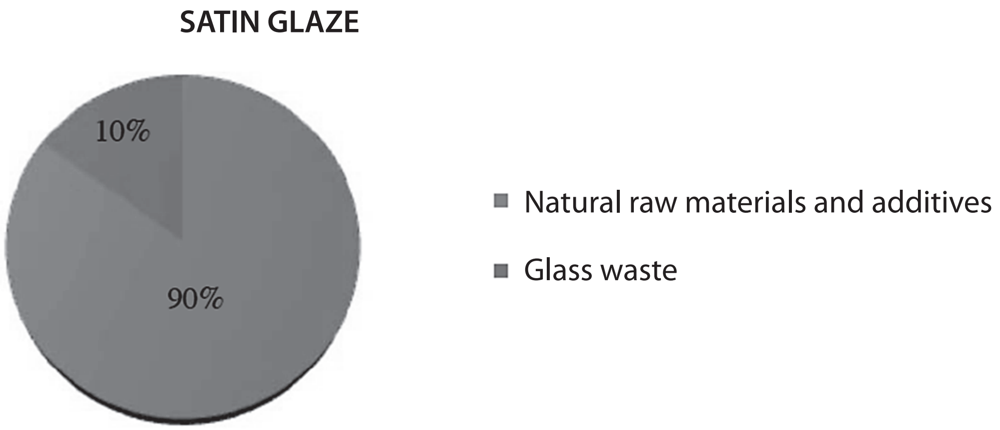

Figure 8. Distribution of the percentage of recycled glass waste used with natural raw materials.

4. CONCLUSIONS

The following conclusions may be drawn from the studies and analyses carried out to obtain an ecological tile in this ECOLOGIC project:

Highly vitrified ceramic bodies (porcelain tile bodies) were obtained by including a 5% fraction by weight of recycled glass waste, together with a further 5% fraction of chamotte and sludge.

An engobe–glaze for porcelain tile bodies was also developed that included recycled glass waste and chamotte. A 'satin' glaze was also successfully developed using different types of recycled glass: 10% (by weight) of a sodium–calcium glass and a further 5% (by weight) of borosilicate glass.

With this method, an integral ecological ceramic tile was manufactured on an industrial scale, in which up to 80% of waste materials were successfully included in the body composition and which provided technical characteristics similar to conventional porcelain tiles.

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